Studies of natural and synthetic agardites

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Abstract

Agardite of formula [(Al,Nd,REE)$Cu_6(AsO_4)_3(OH)_6.3H_2O$] has been discovered at Cobar, New South Wales, Australia. A series of synthetic agardites were analysed by X-ray diffraction and a correlation exists between the effective ionic radius of the REE^{3+} in the M site and the unit cell size for each respective agardite mineral. No value for the effective ionic radius of 9-coordinate Bi^{3+} has been reported but a value of approximately 115.5 pm is estimated from this correlation. The results of the TGA analyses show that the synthetic agardites are all fully hydrated, i.e., n = 3.

Near infrared spectroscopy and mid-infrared spectroscopy has been used to characterise a group of synthetic agardites of formula $ACu_6(AsO_4)_2(OH)_6.3H_2O$ where A is a rare earth element. The hydroxyl stretching region is characterised by four bands observed at around 3568, 3489, 3382 and 3290 cm^{-1}. The first two bands are attributed to the stretching mode of hydroxyl units and the last two bands to water stretching vibrations. The position of these bands indicates strongly hydrogen bonded water. The water in agardites is zeolitic type water. Near-IR spectroscopy shows a series of bands at 7242, 7007, 6809, 6770 and 6579 cm^{-1} attributed to the first

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overtones of the hydroxyl fundamentals. The NIR spectrum of agardite (Sm) is different and may be affected by electronic bands. Combination bands are observed at around 4404, 4343, 4340, 4294 and 4263 cm^{-1}. Bands attributed to water combination modes are found at around 5200, 5173, 5082 and 4837 cm^{-1}. Agardites are a group of minerals known for their REE content and have been rarely studied. NIR spectroscopy is an excellent technique for the characterisation and ready identification of these minerals.

Keywords: agardite, goudeyite, mixite, petersite, near-IR spectroscopy

Introduction

There are a wide variety of techniques that are available to the mineral scientist for obtaining molecular information. Among these techniques are the techniques of vibrational spectroscopy. These vibrational spectroscopic techniques include both Raman and infrared spectroscopy. Among the infrared spectroscopic techniques, there are (a) the absorption (KBr) technique, (b) the infrared emission technique (IES), (c) the reflectance techniques including diffuse and specular reflectance, (d) attenuated total reflectance (ATR), (e) infrared microscopy and (f) photoacoustic FTIR spectroscopy (PAS). In particular the selection of the technique depends on the particular problem in hand. For example infrared emission spectroscopy is suitable for studying dehydroxylation and the thermal changes in minerals at the elevated temperatures. The pressing of a KBr pellet with minerals may alter the spectrum through absorption or exchange of the potassium into the mineral structure. ATR is useful for powders but is limited by the signal to noise

ratio determined by the energy throughput. PAS is a non-destructive technique useful for handling irregular shaped minerals but is limited by the number of samples that may be handled in a given period of time. Specular reflectance is not readily applicable to most minerals as the technique normally applies to flat, shiny polished surfaces although specular infrared reflectance studies have been used to study thermally treated carbon surfaces. The diffuse reflectance technique (DRIFT) is more applicable to powders but is limited to some extent by the Restrahlen effects where the particle size and the incident infrared wavelengths create interference effects. Such effects are minimised by mixing the mineral with KBr at the 5% level. The advantage of using the DRIFT technique is that it provides a rapid technique for analysing samples without any interference through sample preparation. The DRIFT technique avoids the possibility of ion exchange of the potassium ion and non-randomly oriented samples. The technique is particularly useful where the Restrahlen effects are minimal. These effects appear towards the low frequency region normally below 1000 cm^{-1}. Thus the DRIFT technique lends itself to the study of the hydroxyl-stretching region of kaolinites where such effects are not observed. Further such a technique is most useful in the near-IR region. In this work we show the use of NIR spectroscopy for the identification and characterisation of agardite, one of the mixite group of minerals.

Agardite is a member of the mixite group, $ACu_6(AsO_4)_2(OH)_6.3H_2O$ for the fully hydrated formula, with ($A = REE^{3+}$). Mixite (A = Bi), goudeyite (A = Al), zalesiite (A = Ca, with protonation of the lattice for charge compensation) and petersite-(Y), the phosphate analogue of agardite-(Y) are recognized isomorphous species in the group. Of the many possible rare earth congeners constituting the

agardite group, only agardite-(Y) and agardite-(La) are recognized as distinct species by the IMA (ANTHONY et al. 2000). Others have been reported in the literature (BRAITHWAITE & KNIGHT 1990; DUNIN-BARKOVSKAYA 1976; HESS 1983; KRAUSE et al. 1997; OLMI et al. 1988; WALENTA 1960) but their species status remains unresolved. It should be noted that formulae given above refer to ideal, end-member compositions; extensive solid solution in the A site and involving P for As is known for naturally occurring material. Water in the lattice is for the most part thought to be zeolitic in nature, as evidenced by single-crystal X-ray structure determinations. (ARUGA & NAKAI 1985; BAYLISS et al. 1966; MILETICH et al. 1997) The crystal structures of natural mixite and agardite compounds reveal a microporous framework structure (ARUGA & NAKAI 1985; HESS 1983) with a framework similar to that of zeolites. (MILETICH et al. 1997) Dietrich et al. (DIETRICH et al. 1969) originally proposed that the water in agardite was zeolitic. As such these minerals may have potential for catalytic applications.

The mixite group consists of secondary minerals formed through crystallisation from aqueous solution. The conditions under which this crystallisation takes place, particularly relating to anion and cation concentrations, pH, temperature and kinetics of crystallisation, determines the particular mineral that is formed. Recently, Raman spectroscopy has been used to gain an understanding of many properties of secondary minerals (FROST 2003; FROST et al. 2003a; FROST et al. 2003b; FROST & KLOPROGGE 2003; FROST et al. 2003e; MARTENS et al. 2003a; MARTENS et al. 2003b). In particular, Raman spectroscopy has been used to determine paragenetic relationships between many closely related phases (FROST et

al. 2003a; FROST & KLOPROGGE 2003; FROST et al. 2004; FROST et al. 2003c; FROST & WEIER 2003; FROST et al. 2003d). Agardite-(Ce), for example, is the mineral ($CeCu_6(AsO_4)_2(OH)_6.3H_2O$) as such the mineral has two vibrating units which will contribute to the NIR spectra, namely the hydroxyl units and the water HOH units. In this paper we report a Near-infrared spectroscopic analysis of a set of synthetic agardite minerals.

Minerals:

The minerals were checked for phase integrity using powder X-ray diffraction and for chemical composition using an electron probe.

Natural sample

Naturally-occurring agardite was recovered from highly siliceous, oxidized lode material (220-225 RL) in the New Cobar deposit, near Cobar, New South Wales. It occurred as very fine, sky blue needles occasionally forming small, flat sprays, but more commonly as masses of randomly oriented needles. It was found in close association with olivenite, chenevixite, segnitite and partially oxidized arsenopyrite. SEM images of agardite showed the needles to be elongated hexagonal prisms rarely exceeding 500 μm in length and ranging from 2-10 μm in width. Energy dispersive X-ray examination of a number of single crystals of agardite using a Jeol T330 SEM indicated the presence of major Cu, As and Y, corresponding to agardite-(Y), with significant amounts of Nd and minor to trace amounts of La, Sm and Al. Some individual crystals had Nd>Y and these would correspond to agardite-(Nd).

Synthesis of agardites

Pure end-members of the agardite group were synthesized in the following way. To 30 cm^3 of water in a 250 cm^3 Teflon-lined acid digestion bomb was added with stirring 6.0 mmol of $Cu(NO_3)_2.2.5H_2O$, 3.0 mmol of $Na_2HAsO_4.7H_2O$, and 1.0 mmol of $Y(NO_3)_3.6H_2O$. The pH of the mixture was adjusted to 6.6 by dropwise addition of 1.0 M aqueous NaOH. The bomb was sealed and the mixture heated at 180°C for 48 hours, then cooled to room temperature. The product, agardite-(Y), was filtered off, washed with water, then acetone and sucked dry at the pump (yield > 95%). Powder X-ray diffraction using a Phillips PW1825 X-ray diffractometer with Mo Kα radiation showed that a single crystalline phase was present. Separate pure samples of agardite-(La), -(Ce), -(Pr), -(Nd), -(Sm) and -(Eu) were prepared in identical fashion with similar yields by substituting the appropriate hydrated REE nitrate for $Y(NO_3)_3.6H_2O$.

Powder X-ray Diffraction

The most commonly used instrumentation for mineral identification in this study was a Phillips PW1825/20 powder X-ray diffractometer, employing CuKα radiation (λ = 1.5418 Å). In each case a small amount of the material of interest was ground to a fine powder in a mortar and pestle before being placed on the sample stage. A smaller quantity of high purity silicon was added as a standard to those samples that were to have unit cell parameters determined. X-ray traces were produced between 5-70° in 2θ, with a step size of 0.02 and a speed of 0.02° min^{-1}.

Phases were identified from the X-ray traces using Diffraction Technology data processing software (Traces Version 6). Some 140 X-ray traces were produced in identifying various mineral species from the deposit.

Infrared and Near-infrared spectroscopy (NIR)

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000 to 525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Near IR spectra were collected on a Nicolet Nexus FT-IR spectrometer with a Nicolet Near-IR Fibreport accessory. A white light source was used, with a quartz beam splitter and TEC NIR InGaAs detector. Spectra were obtained from 11 000 to 4000 cm^{-1} by the co-addition of 64 scans at a resolution of $8cm^{-1}$. A mirror velocity of 1.2659 was used. The spectra were transformed using the Kubelka-Munk algorithm to provide spectra for comparison with absorption spectra.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken

until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Characterization of Natural Agardite-(Y) from the New Cobar Deposit

A weighed quantity of natural agardite-(Nd) from New Cobar was completely dissolved in analytical grade aqueous HNO_3 and analysed by ICP-MS for Cu, As, P, Y, La, Ce, Pr, Nd, Sm, Eu, Bi, Al, Ca, and Pb, in order to determine the exact composition of the mineral. Analyses were carried out by the Australian Government Analytical Laboratories (AGAL), Pymble, NSW.

Insert Table 1 here.

Agardite-(Nd) **$(Al,Nd,REE)Cu_6(AsO_4)_3(OH)_6.3H_2O$**

Although bulk chemical analysis shows that the dominant rare earth in New Cobar agardite is yttrium, qualitative analysis by SEM on many individual crystals suggests that a phase representing agardite-(Nd) also exists in the deposit (Table 1). This find represent the first known Australian occurrence of the phase, although material described as agardite-(Nd) has been reported from several localities in Germany (WALENTA 1960; WALENTA 1970; WALENTA 1995) and a single locality in England (EMBREY & SYMES 1987). The neodymium-rich variety of agardite has not as yet been accepted as a separate mineral species by the International Mineralogical Association (IMA), and thus the name "agardite-(Nd)" is only used in a descriptive sense. The minerals agardite-(Y) and agardite-(La) are at present the only accepted species in the agardite group (ANTHONY et al. 2003).

Agardite and Associated Minerals

Agardite belongs to the mixite group. Minerals in this group are hexagonal and have the general formula $MCu_6(XO_4)_3(OH)_6.nH_2O$, where M = Bi, REE^{3+}, Al, or Ca, X = As or P and $n \leq 3$ (ARUGA & NAKAI 1985; MILETICH et al. 1997; OLMI et al. 1991). Names and formulae of approved minerals in this group are given in Table 2 (After (OLMI et al. 1991; SEJKORA et al. 1999).The discovery of agardite-(Y) (and probably agardite-(Nd)) in the oxidised zone of the New Cobar deposit prompted a closer look at the group as a whole. Results from the unit cell refinement

of the synthetic agardite group minerals using LAPOD (LANGFORD 1971; LANGFORD 1973) are summarised in Table 2.

Insert Table 2 here

Insert Table 3 here

Insert Figure 1 here

The "M" site in the formula above is a 9-coordinate tri-capped trigonal prismatic site that can accommodate a wide variety of different metal cations (ARUGA & NAKAI 1985; HESS 1983; MEREITER & PREISINGER 1986; MILETICH & ZEMANN 1993; MILETICH et al. 1997).Closer inspection of the results above reveals that a correlation exists between the effective ionic radius of the REE^{3+} in the M site and the unit cell size for each respective agardite mineral. Figure 1 shows a plot of these two parameters, with the size of the 9-coordinate ionic radii being taken from (SHANNON 1976).No value for the effective ionic radius of 9-coordinate Bi^{3+} has been reported in the literature, and as such mixite could not be included on the plot. The graph does, however, allow this value to be approximated as unit cell parameters for pure, synthetic mixite have been determined, and extrapolation from the graph yields a value of approximately 115.5 pm. The plot may potentially be used for predicting the predominant rare earth elements in natural

agardite specimens, although substantial substitution in the site by calcium, aluminium or lead may complicate this procedure. Data for petersite-(Y) are included in the Table 2. It is noted that the phosphate unit cell is somewhat smaller than related arsenates, as expected. Without data for other potential members of the group, no further comparison is possible.

Several authors (ARUGA & NAKAI 1985; MILETICH et al. 1997; SEJKORA et al. 1999) have commented upon the nature of the water of hydration in mixite group minerals. It has been found that the water is zeolitic in nature and exhibit reversible hydration behaviour. It was considered necessary, therefore, to determine the degree of hydration in the agardite group minerals produced synthetically. The result of the TGA analyses, given in Table 4, show that the synthetic agardites are all fully hydrated, i.e., n = 3. The fact that in all cases the number of waters calculates for greater than three is either a result of the presence of a small quantity of adsorbed water in the products or partial decomposition of arsenate, AsO_4^{3-}, to pyroarsenate, $As_2O_7^{4-}$.

Insert Table 4 here

Agardite-(Ce), for example, is the mineral ($CeCu_6(AsO_4)_2(OH)_6.3H_2O$) and three different vibrating units will contribute to the overall spectroscopic profile, namely the OH groups, the water molecules and the AsO_4 groups. The first two vibrating species will contribute to the high wavenumber region whilst the AsO_4 units will show Raman bands below 1200 cm^{-1}. It has been shown that the water can be reversibly lost and the number of water molecules per formula unit can vary up to 3.

According to Mereiter and Preisinger (1986) mixites have a microporous framework structure based upon $(M^{3+})_{1-x}(M^{2+})_xCu_6(OH)_6(AsO_4)_{3-x}(AsO_3OH)_x$. (MEREITER & PREISINGER 1986), with vacancies in the A site or substitution by divalent cations being compensated by protonation of the lattice. On the spectroscopic time scale, exchange of protons between water molecules and arsenate ions is also likely. According to this formulation two types of units involving As are found, namely AsO_4 and $HAsO_4$. The spectra of the first overtone of the hydroxyl fundamentals of a series of synthetic agardites are shown in Figure 2. The results of the band component analyses are reported in Table 5 The spectra for the mixites of Ce, La, Y, Eu are very similar, although subtle differences in the spectra may be observed. However the NIR spectrum of the agardite of Sm is very different. One possibility is that electronic bands are overlapping with the NIR bands. In general bands are observed in around the same positions for Ce, La, Y and Eu. Five bands are observed at around 7242, 7007, 6809, 6770 and 6579 cm^{-1}.

The infrared spectra of the hydroxyl stretching region of the synthetic agardites are shown in Figure 3. There is a striking similarity between the spectra of the hydroxyl stretching region. The bands are found in the same position for all five agardites and only some variation in intensity of the bands is observed for the different REE agardites. Infrared bands are observed at around 3568, 3489, 3382 and 3290 cm^{-1}. The first two bands are attributed to hydroxyl stretching vibrations and the last two to water HOH stretching bands. The region of the combination bands of the hydroxyl vibrations is shown in Figure 4. Again there is a remarkable similarity between the spectra. Only some subtle variations in intensity of the component bands are observed. Bands are observed at 4404, 4343, 4340, 4294 and 4263 cm^{-1} for

agardite-(Ce). Two additional bands are observed at 4174 and 4085 cm^{-1}. These bands are common to all the agardite spectra in this region.

The NIR spectra of the water HOH overtone region are shown in Figure 5. The spectra are strikingly similar except for agardite (Eu). For agardite-(Ce) bands are observed at 5383, 5318, 5201, 5173, 5082 and 4837 cm^{-1}. The most intense band is the band at around 5082 cm^{-1}. The spectrum of agardite (Eu) appears different. Additional bands are observed at 4587 and 4551 cm^{-1}. The exact origin of these bands is not known. If we use the formula $(M^{3+})_{1-x}(M^{2+})_xCu_6(OH)_6(AsO_4)_{3-x}(AsO_3OH)_x$ two types of units containing As exist, namely AsO_4 and $HAsO_4$. It is possible that units of H_3O^+ are formed and these types of water contribute to the spectral profile in the 4500 to 5500 cm^{-1} region of agardite (Eu). The agardite-(Sm) mineral displayed some electronic spectra in the NIR region (Figure 6).

Conclusions

A natural agardite-(Nd) has been found in the new Cobar deposit, Cobar, New South Wales, Australia. Although bulk chemical analysis shows that the dominant rare earth in New Cobar agardite is yttrium, qualitative analysis by SEM on many individual crystals suggests that a phase representing agardite-(Nd) also exists in the deposit. This find represent the first known Australian occurrence of the phase.

Near-IR spectroscopy is a technique, which has not been previously applied to the study of mixites. Mixites a group of minerals with known REE content which

have been rarely studied. Indeed mixites by their very nature, being composed of zeolitic water and hydroxyls bonded to Cu, lend themselves to study by NIR. NIR reflectance techniques have proven must useful for the analysis of mixites. Three Near–IR spectral regions are identified: (a) the high wavenumber region between 6400 and 7400 cm^{-1} attributed to the first overtone of the fundamental hydroxyl stretching mode (b) the 4800-5400 cm^{-1} region attributed to water combination modes of the hydroxyl fundamentals of water, and (c) the 4000-4800 cm^{-1} region attributed to the combination of the stretching and deformation modes of the MOH units of the mixites. NIR spectroscopy enables the separation of the hydroxyl bands of the water and M-OH units for the mixites. In particular, whereas the overlap of the hydroxyl stretching frequencies of water and the MOH units overlap in the mid-IR, such overlap does not occur in the Near-IR. NIR spectroscopy enables the separation of these hydroxyl modes.

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Table 1 Analytical data (wt%) for bulk agardite[a].

Element (as oxide)	**Observed**	**Calculated**[b]
CuO	46.10	46.15
As_2O_5	32.34	32.39
P_2O_5	0.22	0.23
Al_2O_3	1.83	1.83
CaO	0.38	0.38
Ce_2O_3	0.02	0.02
Eu_2O_3	0.10	0.11
La_2O_3	0.17	0.17
PbO	2.84	2.83
Nd_2O_3	1.95	1.98
Pr_2O_3	0.31	0.31
Sm_2O_3	0.45	0.46
Y_2O_3	2.67	2.68
H_2O		10.46
Total		100.00

[a]Plus 98 ppm Bi. Analysis on 1.25 mg less 0.26 mg insoluble. [b] Calculated for $\{[Y_{0.245}Nd_{0.122}Sm_{0.027}Pr_{0.019}La_{0.011}Eu_{0.006}Ce_{0.001}]Al_{0.372}Pb_{0.131}Ca_{0.070}\}$-$Cu_6\{(As_{2.915}P_{0.033})O_4\}_3(OH)_6.3H_2O$.

Table 2 Names and formulae of mixite group minerals.

Name	Formula
Mixite	$BiCu_6(AsO_4)_3(OH)_6.3H_2O$
Agardite-(Y)	$(Y,Ca)Cu_6(AsO_4)_3(OH)_6.3H_2O$
Agardite-(La)	$(La,Ca)Cu_6(AsO_4)_3(OH)_6.3H_2O$
Zálesíite	$(Ca,REE)Cu_6(AsO_4)_3(OH)_6.3H_2O$
Goudeyite	$(Al,REE)Cu_6(AsO_4)_3(OH)_6.3H_2O$
Petersite-(Y)	$(Y,Ca)Cu_6(PO_4)_3(OH)_6.3H_2O$

Table 3 Refined unit cell parameters with standard deviations in parentheses for synthetic mixite group minerals with end-member compositions.

Species	a (pm)	c (pm)	Volume x10^6 (pm^3)
Agardite-(Y)	1354.9 (2)	587.7 (1)	934.4 (2)
Agardite-(Eu)	1360.7 (3)	590.4 (3)	946.6 (3)
Agardite-(Sm)	1362.2 (3)	590.4 (2)	948.7 (2)
Agardite-(Nd)	1364.2 (3)	592.4 (2)	954.8 (2)
Agardite-(Pr)	1366.2 (3)	593.1 (2)	958.8 (2)
Agardite-(Ce)	1368.3 (3)	592.9 (2)	961.4 (3)
Agardite-(La)	1371.2 (3)	594.3 (3)	967.8 (2)
Mixite	1364.1 (3)	590.4 (3)	948.7 (2)
Petersite-(Y)	1318.9 (3)	584.7 (2)	880.7 (3)

Table 4 Analytical results of thermogravimetric analysis.

Species	Weight Loss (%)	No. of Waters
Agardite-(Y)	5.32	3.10
Agardite-(La)	5.99	3.69
Agardite-(Ce)	5.85	3.61
Agardite-(Pr)	6.25	4.36
Agardite-(Nd)	5.60	3.89
Agardite-(Sm)	5.95	4.17
Agardite-(Eu)	5.51	3.42

Table 5 Results of the near infrared and infrared spectral analysis of synthetic mixites

Ce	La	Y	Eu	Sm
Band Centre (cm^{-1}) / Intensity (%)	**Band Centre (cm^{-1}) / Intensity (%)**	**Band Centre (cm^{-1}) / Intensity (%)**	**Band Centre (cm^{-1}) / Intensity (%)**	**Band Centre (cm^{-1}) / Intensity (%)**
				9205 / 2.84 9132 / 0.73 9060 / 1.70 8971 / 0.07
				8080 / 1.19 8023 / 1.56 7938 / 7.00 7860 / 2.40
7242 / 0.06 7007 / 3.45 6809 / 5.67 6770 / 1.48 6579 / 0.42	7173 / 0.01 7014 / 2.90 6815 / 7.20 6772 / 0.87 6560 / 0.32	7004 / 2.77 6933 / 0.75 6850 / 1.08 6755 / 4.63 6588 / 0.67	7022 / 2.10 6912 / 1.57 6778 / 3.67 6759 / 0.74 6561 / 0.28	7196 / 1.23 7137 / 4.44 7062 / 0.84 7009 / 6.83 6983 / 1.06 6764 / 3.64 6652 / 0.26 6543 / 6.38 6472 / 1.13 6410 / 0.13 6208 / 0.31
5383 / 0.12 5318 / 0.27 5201 / 9.27 5173 / 9.05 5082 / 33.51 4837 / 2.62	5198 / 8.81 5161 / 10.49 5076 / 30.89 4810 / 1.95	5200 / 8.35 5141 / 8.83 5095 / 24.66 4852 / 2.66	5380 / 0.06 5194 / 9.95 5110 / 27.77 5007 / 1.27 4921 / 1.84 4904 / 10.67 4776 / 0.68	5310 / 0.73 5197 / 9.09 5117 / 13.73 4998 / 6.92 4837 / 2.53
			4587 / 1.30 4551 / 0.37	4588 / 0.10
4404 / 2.51 4343 / 3.54 4340 / 12.40 4294 / 10.40 4263 / 1.15	4406 / 2.74 4344 / 12.71 4342 / 1.28 4292 / 14.84 4252 / 1.07	4394 / 7.64 4357 / 6.49 4340 / 3.98 4303 / 22.10	4404 / 3.47 4357 / 8.67 4339 / 2.89 4301 / 17.75	4405 / 2.08 4343 / 7.23 4297 / 8.05 4265 / 1.89
4174 / 3.66 4085 / 0.41	4172 / 3.44 4086 / 0.49	4173 / 5.18 4082 / 0.20	4173 / 4.47 4083 / 0.47	4172 / 3.51 4087 / 0.42
3568 / 1.79 3489 / 10.12 3382 / 24.30 3290 / 31.17	3565 / 2.47 3489 / 9.63 3388 / 26.61 3277 / 23.50	3568 / 3.24 3482 / 11.06 3362 / 26.45 3296 / 25.81	3567 / 3.86 3485 / 11.21 3371 / 29.23 3251 / 19.46	3567 / 3.55 3487 / 12.72 3376 / 28.46 3252 / 17.40

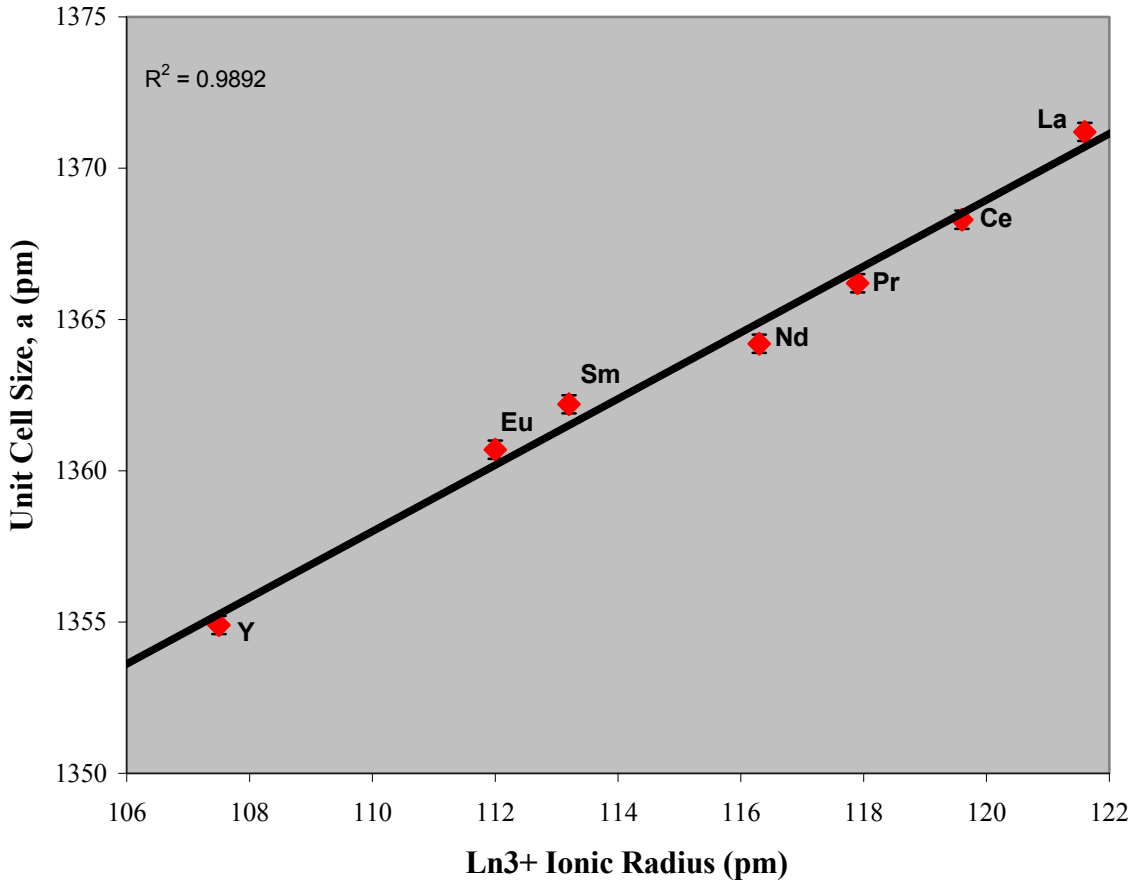
R^2 = 0.9892
La
Ce
Pr
Nd
Sm
Eu
Y
1375
1370
1365
1360
1355
1350
106
108
110
112
114
116
118
120
122
Unit Cell Size, a (pm)
Ln3+ Ionic Radius (pm)

Figure 2

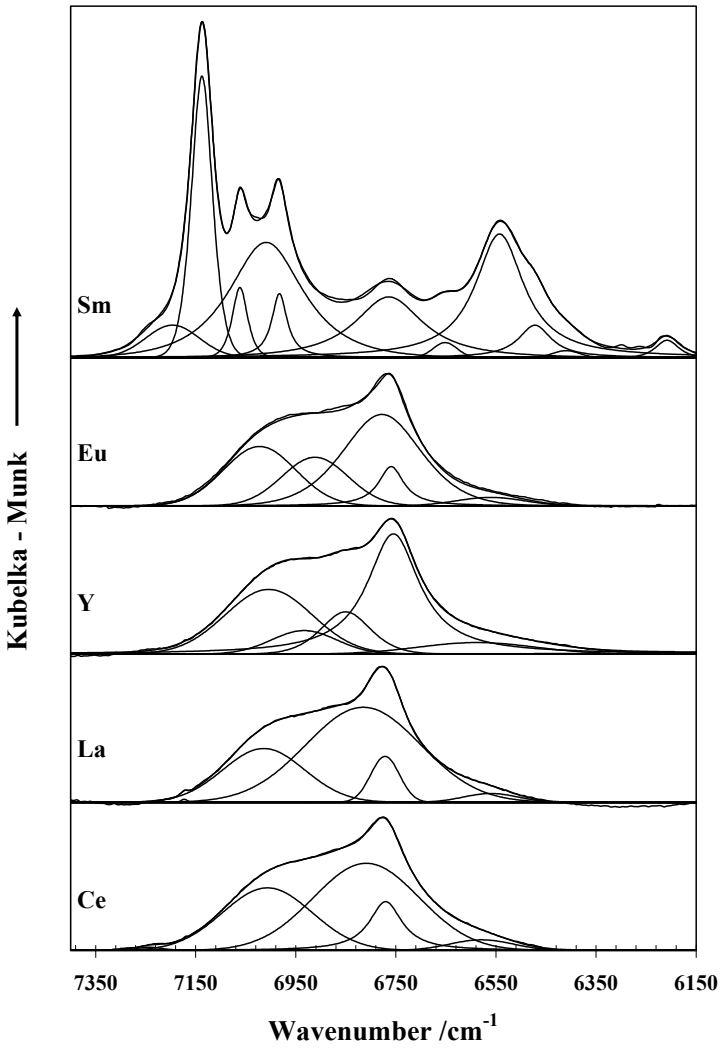
Sm
Eu
Y
La
Ce
Kubelka - Munk
7350
7150
6950
6750
6550
6350
6150
Wavenumber /cm-1

Figure 3

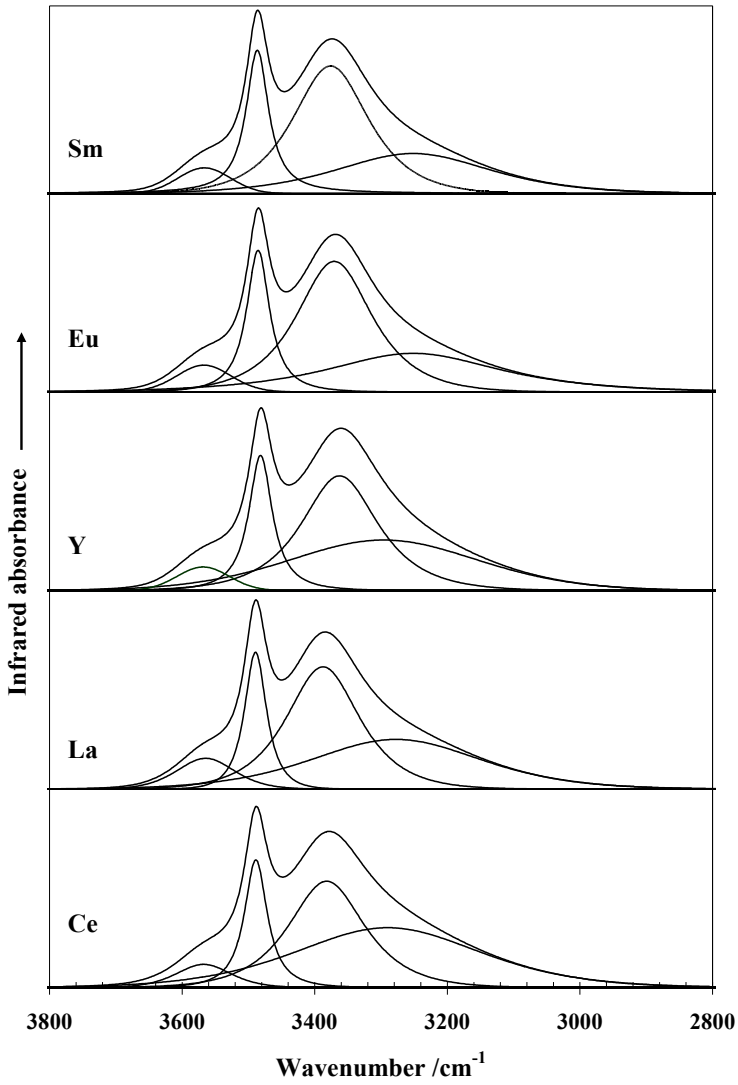
Sm
Eu
Y
La
Ce
Infrared absorbance
3800
3600
3400
3200
3000
2800
Wavenumber /cm-1

Figure 4

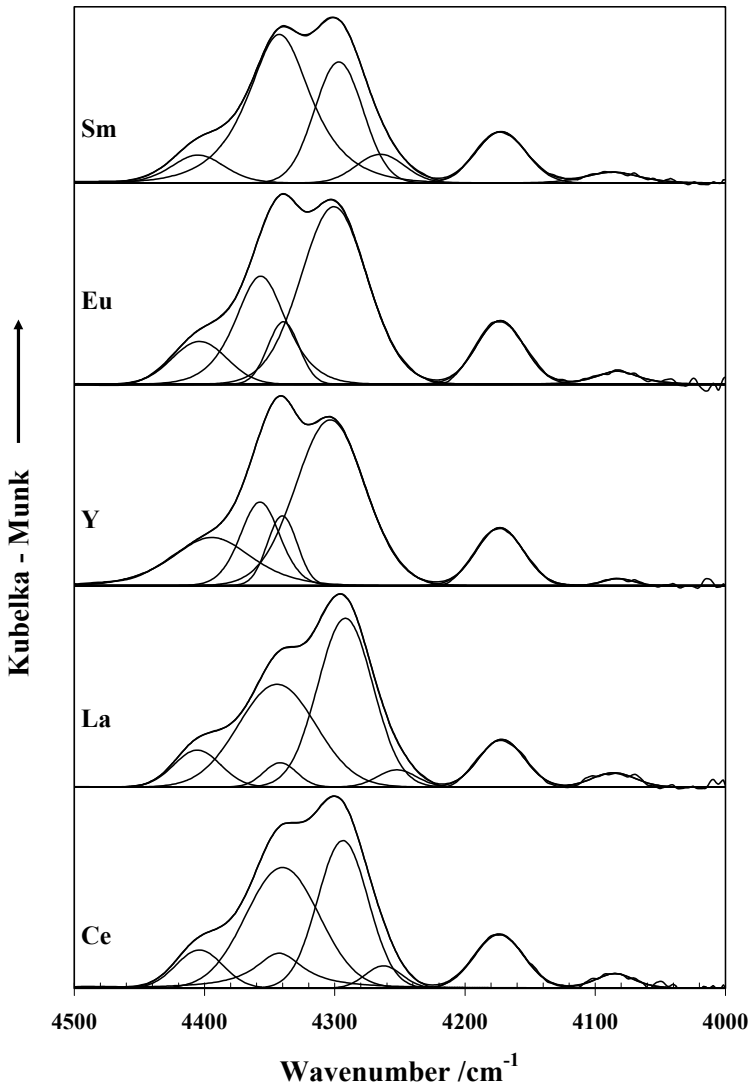
Sm
Eu
Y
La
Ce
Kubelka - Munk
4500
4400
4300
4200
4100
4000
Wavenumber /cm-1

Figure 5

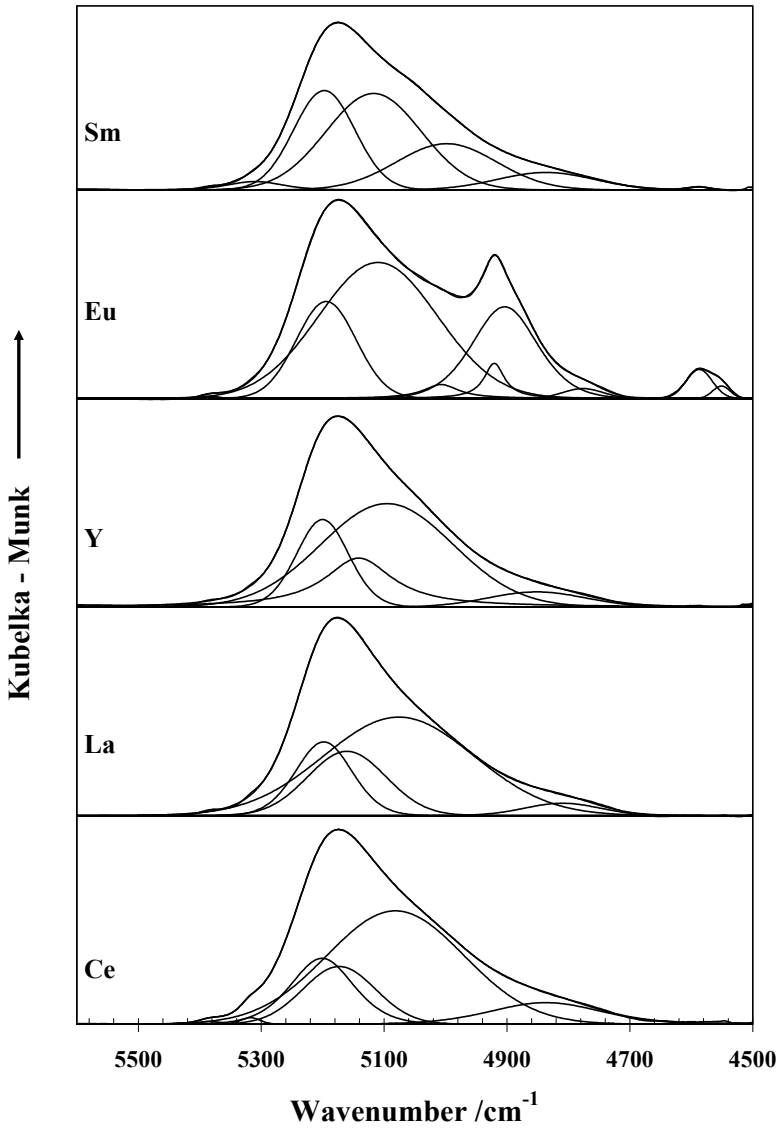
Sm
Eu
Y
La
Ce
Kubelka - Munk
5500
5300
5100
4900
4700
4500
Wavenumber /cm-1

Figure 6